Nitrous oxide in the surface layer of the tropical North Atlantic Ocean along a west to east transect

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[1] Nitrous oxide (N_2O) was measured during the first German SOLAS (Surface Ocean – Lower Atmosphere Study) cruise in the tropical North Atlantic Ocean on board R/V *Meteor* during October/November 2002. About 900 atmospheric and dissolved N_2O measurements were performed with a semi-continuous GC-ECD system equipped with a seawater-gas equilibrator. Surface waters along the main transect at 10°N showed no distinct longitudinal gradient. Instead, N_2O saturations were highly variable ranging from 97% to 118% (in the Guinea Dome Area, 11°N, 24°W). When approaching the continental shelf of West Africa, N_2O surface saturations went up to 113%. N_2O saturations in the region of the equatorial upwelling (at 0–1.5°N, 23.5–26°W) were correlated with decreasing sea surface temperatures and showed saturations up to 109%. The overall mean N_2O saturation was 104 ± 4% indicating that the tropical North Atlantic Ocean is a net source of atmospheric N_2O. *INDEX TERMS:* 4820 Oceanography: Biological and Chemical: Gases; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks. **Citation:** Walter, S., H. W. Bange, and D. W. R. Wallace (2004), Nitrous oxide in the surface layer of the tropical North Atlantic Ocean along a west to east transect, *Geophys. Res. Lett.*, *31*, L23S07, doi:10.1029/2004GL019937.

1. Introduction

[2] Nitrous oxide (N_2O) is an important atmospheric trace gas because it influences, directly and indirectly, the Earth's climate to a significant degree: In the troposphere, it acts as a greenhouse gas with a relatively long atmospheric lifetime [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001] whereas in the stratosphere it is the major source for nitric oxide radicals, which are involved in one of the main ozone reaction cycles [*World Meteorological Organization*, 2003]. Published source estimates indicate that the world's oceans play a major role in the global budget of atmospheric nitrous oxide [*IPCC*, 2001]. Generally, oligotrophic areas seem to be near equilibrium with the atmosphere, whereas coastal and equatorial upwelling areas show enhanced N_2O concentrations [*Nevison et al.*, 1995; *Suntharalingam and Sarmiento*, 2000]. Here we present about 900 measurements of dissolved and atmospheric N_2O during the first German SOLAS (Surface Ocean – Lower Atmosphere Study) cruise. It is the first high-resolution data set of N_2O in the tropical North Atlantic Ocean along a West to East transect and it is complementary to previous N_2O measurements of *Oudot et al.* [1990, 2002] and *Weiss et al.* [1992].

[3] The cruise took place on board R/V *Meteor* (expedition no. M55) from Willemstad (Curaçao, Netherl. Antilles) to Douala (Cameroon) from 12 October to 17 November 2002. The cruise track consisted of two main transects: (i) The West to East transect along 10–12°N covering the oligotrophic tropical North Atlantic Ocean and the continental shelf area of the West African coast off Guinea Bissau and (ii) a shorter West to East transect along the equatorial upwelling (Figure 1).

2. Method

[4] N_2O was determined with a gas chromatograph equipped with an electron capture detector. Further details of the analysis system are described in *Bange et al.* [1996]. A series of measurements of atmospheric N_2O and N_2O in seawater-equilibrated air followed by two standards was repeated every 50 min. Mixtures of N_2O in synthetic air were used to obtain two-point calibration curves. The mixtures used contained 311.7 ± 0.1 and 346.5 ± 0.2 ppb N_2O, respectively. These are gravimetrically prepared gas mixtures (Deuste Steininger GmbH, Mühlhausen Germany) and have been calibrated against the NOAA (National Oceanic and Atmospheric Administration, Boulder, Co.) standard scale in the laboratories of the Air Chemistry Division of Max Planck Institute for Chemistry Mainz, Germany. The precision, calculated as the ratio of the standard deviation of the atmospheric measurements and the mean atmospheric mixing ratio, was 0.8%.

[5] Seawater was pumped continuously from a depth of 4 m into a shower-type equilibrator developed by R. F. Weiss (Scripps Institution of Oceanography, La Jolla, Ca.). N_2O concentrations (C, in nmol L^{-1}) were calculated by applying the solubility equation of *Weiss and Price* [1980]:

$$C = \beta(T,S)x'P,$$

where x' is the measured N_2O dry mole fraction, P is the atmospheric pressure, and β is the solubility coefficient, which is a function of the water temperature (T) and salinity (S). Time series of seawater temperature (SST), salinity, wind speed, and atmospheric pressure were obtained from the ship's records. Differences between the seawater temperature at the seawater intake and the continuously recorded water temperature in the equilibrator were corrected:

$$C_w = C\,\beta(T_{eq})/\beta(SST)$$

with $\beta(SST)$ and $\beta(T_{eq})$ representing the N_2O solubility at seawater temperature and water temperature inside the

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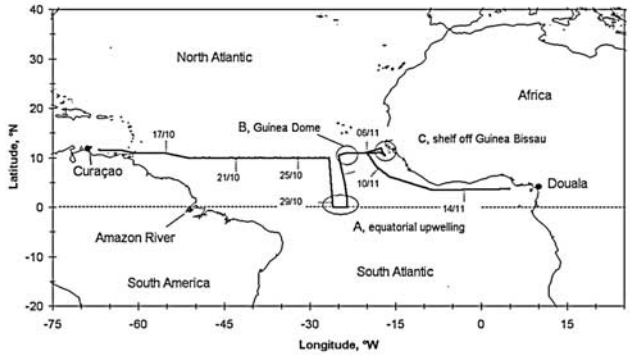

Figure 1. Cruise track of M55 in October–November 2002. N_2O measurements were started 17 October and were finished 14 November. Areas of special interest discussed in the text are marked.

equilibrator at the time of the measurement, respectively. N_2O saturations (*Sat*) in % (i.e., 100% = equilibrium) were calculated as follows:

$$Sat = 100\, C_w / C_a$$

where C_a is the equilibrium concentration of dissolved N_2O based on the actual measurement of ambient air (see above). The mean relative errors of the N_2O concentrations and saturations were calculated to be 1.2% and 1.6%, respectively (details of the error propagation computation are given by *Bange et al.* [2001]).

3. Results and Discussion

[6] The mean atmospheric N_2O dry mole fraction was 318 ± 3 ppb. Due to the seasonal northward shift of the Intertropical Convergence Zone to about 10°N, the origin of the air masses sampled during the cruise were from both the northern and the southern hemisphere. 4-days air mass back trajectories (provided by the German Weather Service, Offenbach, Germany) indicated that air masses sampled at latitudes south of 7°N originated from the southern hemisphere. Based on this classification we computed mean N_2O values for northern and southern hemisphere air masses of 319 ± 3 ppb and 317 ± 2 ppb, respectively. The observed atmospheric values are in agreement with N_2O measurements at the baseline monitoring stations Ragged Point, Barbados and Cape Grim, Tasmania. Monthly mean values were 317 ppb (Cape Grim) and 318 ppb (Ragged Point) for October/November 2002. These values were taken from the Advanced Global Atmospheric Gases Experiment (AGAGE) data set (updated version from November 2003) [*Prinn et al.*, 2000]. AGAGE data are available from the anonymous ftp site ftp://cdiac.esd.ornl.edu (subdirectory pub/ale_gage_Agage/Agage/gc-md/monthly) at the Carbon Dioxide Information Analysis Center in Oak Ridge, Tennessee.

[7] N_2O saturations along the main cruise track ranged from 97% to 118% and the SST was generally between 27 and 30°C (Figure 2). Since the main cruise track was located between the eastward flowing North Equatorial Countercurrent (NECC) and the westward flowing North Equatorial Current (NEC) [*Stramma and Schott*, 1999], we crossed several times meandering waters of different origins causing a high variability of the N_2O saturation: Low N_2O saturations of about 100% observed around 24 Oct., 27–28 Oct., and 2 Nov. were generally associated with decreases in salinity (Figure 2). This results from the retroflection of the North Brazil Current, which advects Amazon plume waters (with low N_2O, see below) eastward into the NECC [*Fratantoni and Glickson*, 2002]. Freshwater influences were observed twice: First, at around 50°E (19 Oct., Figure 2) when we crossed the northern boundary of the Amazon river plume (minimum salinity 32.14) and second, on the continental shelf off West Africa where we measured a drop in salinity down to 31.30 (5–6 Nov., Figure 2). N_2O saturations were not enhanced in the Amazon River plume, whereas an increase in N_2O saturations up to 113% were observed on the West African shelf. The low N_2O saturations in the Amazon River plume were attributed to the fact that N_2O-rich waters from the Amazon River are N_2O-depleted because of outgasing to the atmosphere and mixing with near-equilibrium oceanic waters while distributed to the North [*Oudot et al.*, 2002]. The high N_2O saturations on the continental African shelf might result from N_2O-rich riverine waters or groundwater seepage, but not from coastal upwelling as indicated by the uniform SSTs. N_2O saturations up to 118% were observed in the area of the Guinea Dome at 11°N, 24°E (3–4 Nov., Figure 2) which is well-known for pronounced Ekman upwelling [*Siedler et al.*, 1992; *Signorini et al.*, 1999]. In the equatorial region (0–1.5°N, 28–30 Oct., Figure 2) SSTs dropped well below 27°C and were associated with enhanced N_2O saturations (up to 109%). We found a good

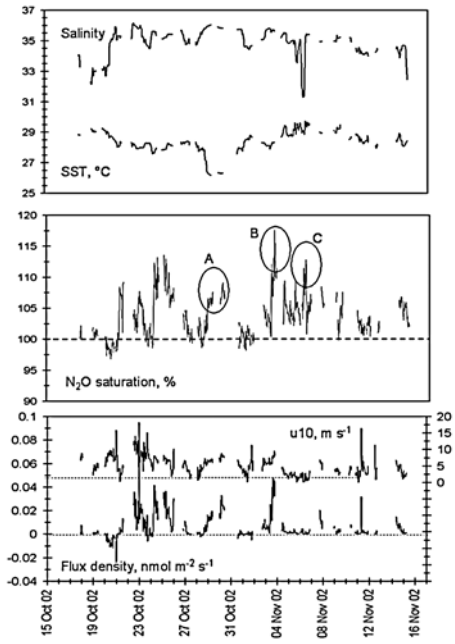

Figure 2. Salinity, seasurface temperature (SST), N_2O saturation, wind speed in 10 m height (u10), and N_2O flux density during M55. Area of special interest discussed in the text are marked (see Figure 1): A, equatorial upwelling; B, Guinea Dome; C, shelf off West Africa (water depths <200 m).

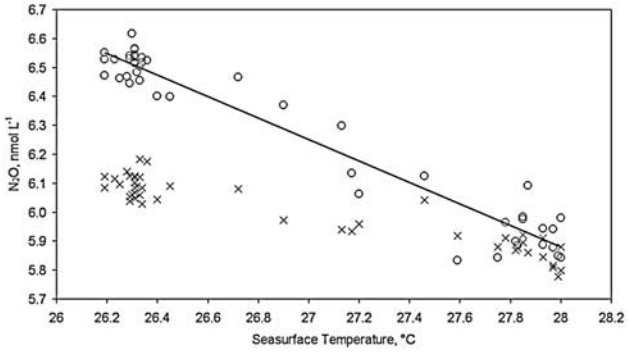

Figure 3. Correlation ($r^2 = 0.94$, n = 46) of SST and N_2O concentration in the equatorial upwelling area (0–2°N, 23.5–26°W). Open circles stand for in-situ measurements and crosses stand for the corresponding equilibrium concentrations calculated as a function of the actual SST, Salinity, atmospheric dry mole fraction, and ambient pressure.

correlation between N_2O concentrations and SST in the equatorial upwelling region (Figure 3) indicating that the enhanced surface N_2O saturations were resulting from upwelling of N_2O-enriched subsurface waters.

[8] In order to account for the NECC/NEC system and the observed N_2O features we defined two latitudinal aligned open ocean regions and a shelf region: 1) the tropical North Atlantic ranging from 1.5–12°N with SST >27°C, 2) the equatorial upwelling from 0–1.5°N with SST <27°C, and 3) the shelf area off the West African coast (water depth <200 m). An overview of the regional mean concentrations and saturations is given in Table 1. The mean N_2O concentrations and saturations of the shelf and equatorial regions are significantly enhanced compared to the 1.5–12°N region. The high variability calculated for the tropical North Atlantic region is biased by the complex hydrography, which is influenced by the Amazon plume, the NECC/NEC system and the Guinea Dome upwelling with highly variable N_2O concentrations. However, a more detailed regional analysis is hampered by the limited data set.

[9] Our data from the tropical North Atlantic are in agreement with previously published data. Recently, *Oudot et al.* [2002] reported a mean N_2O saturation of 108 ± 3%, mainly measured along two transects at 7.5°N and 4.5°S during January–March 1993. They also observed a trend towards enhanced values when approaching the West African coast (up to 118%). In a previous study in the Guinea Dome area during June–August 1986, *Oudot et al.* [1990] observed mean N_2O saturations in the range from 126 ± 5 to 132 ± 6% which are considerably higher than our results (Table 1). In the period from 1979 to 1989, *Weiss et al.* [1992] took part in several measurement campaigns with cruise tracks across the tropical North Atlantic Ocean. Their N_2O measurements are in good agreement with the results presented here. For example, the mean N_2O saturation during the first part of the TTO/TAS leg 3 in February 1983, which covered two transects along 9.5°N (from 20.25 to 28°W) and 28°W (from 9.5 to the equator), was about 105%. Enhanced values during TTO/TAS leg 3 were observed on the coast off Guinea-Bissau (up to 179%) and in the equatorial upwelling (up to 111%). In contrast to our measurements, the high N_2O values observed off Guinea Bissau were caused by coastal upwelling (SST <27°) [*Weiss et al.*, 1992]. Summarizing the results from various N_2O measurements in the open tropical North Atlantic, we found only slight differences (with the exception of the data from the Guinea Dome area by *Oudot et al.* [1990]). Significant differences as found for the Guinea Dome might be caused by seasonal variability of the circulation patterns [*Stramma and Schott*, 1999] in connection with different spatial data coverage. Since coastal upwelling was absent during our cruise, N_2O saturations on the shelf off West Africa were comparably low.

4. N_2O Air-Sea Exchange

[10] The air–sea exchange flux density (F) was parameterized as

$$F = k_w(u)(C_w - C_a),$$

where k_w (in m s^{-1}) is the gas transfer coefficient as a function of wind speed (u in 10 m height), C_w is the measured N_2O seawater concentration, and C_a is the equilibrium N_2O concentration in seawater based on the measured atmospheric value (for calculation of C_w and C_a see Methods section). To calculate k_w, we used the combined linear and quadratic $k_w - u$ relationship from *Nightingale et al.* [2000] (N00):

$$k_w = 9.25\ 10^{-7}\,u + 6.17\ 10^{-7}\,u^2.$$

The N00 relationship shows a dependence on wind speeds intermediate between the commonly used relationships of *Liss and Merlivat* [1986] and *Wanninkhof* [1992]. The measured wind speeds were normalized to 10 m height by using the relationship of *Garratt* [1977]. k_w was adjusted by multiplying with $(Sc/600)^{-0.5}$, where Sc is the *Schmidt* number for N_2O. Sc was calculated using empirical

Table 1. Mean N_2O Concentrations, Saturations, and Flux Densities During M55[a]

	Overall Mean (n = 451)	0–1.5°N (n = 27)	1.5–12°N (n = 416)	Shelf (n = 8)
Concentration, nmol L^{-1}	6.00 ± 0.24	6.49 ± 0.07	5.27 ± 0.20	6.31 ± 0.11
Saturation, %	104 ± 4	107 ± 1	103 ± 3	110 ± 2
Flux density, nmol m^{-2} s^{-1}	0.007 ± 0.011	0.018 ± 0.006	0.006 ± 0.011	0.002 ± 0.002

[a]Values are given as mean ± 1sd. Number of measurements is given in parenthesis.

equations for the kinematic viscosity of seawater [*Siedler and Peters*, 1986] and the diffusion coefficient of N_2O in water. N_2O diffusion coefficients (D_{N2O} in $m^2\ s^{-1}$) were calculated with the equation derived from a compilation of actual measurements [*Rhee*, 2000]:

$$D_{N2O} = 3.16 \times 10^{-6} \exp(-18370/RT),$$

where T is the water temperature in K and R is the universal gas constant. The commonly used equation for D_{N2O} by *Broecker and Peng* [1974] was replaced since *Rhee*'s [2000] equation provides a more reasonable fit with a considerably reduced uncertainty of less than 10% [*Rhee*, 2000]. Flux densities calculated with the above equation are lower by about 10% when compared to computations with *Broecker and Peng*'s [1974] equation [*Bange et al.*, 2001]. We did not apply a correction of D_{N2O} for seawater since the effect of seawater on the diffusion of dissolved gases is not uniform [*King et al.*, 1995] and, to our knowledge, no measurements of the N_2O diffusion in seawater have been published.

[11] The regional mean flux densities clearly reflect the interplay of saturation and wind speeds (Figure 2 and Table 1). In the equatorial region enhanced N_2O saturations and comparably high wind speeds result in high flux densities, whereas over the shelf enhanced N_2O saturations were associated with very low wind speed resulting in low flux densities (Figure 2). The mean flux density of the tropical North Atlantic region is biased by the high variability of both N_2O saturations and wind speeds. The overall mean N_2O flux density was 0.007 ± 0.011 nmol $m^{-2}\ s^{-1}$ which is at the lower end of previously published flux densities: *Oudot et al.* [1990, 2002] computed overall mean flux densities of 0.013–0.021 nmol $m^{-2}\ s^{-1}$ and 0.026 ± 0.032 nmol $m^{-2}\ s^{-1}$ for the tropical North and South Atlantic and the Guinea Dome area, respectively. The obvious discrepancy might be caused by different spatial data coverage, seasonal variability of the N_2O concentrations and wind speeds, and the use of different approaches for the transfer coefficient k_w.

5. Summary

[12] N_2O saturations in the tropical North Atlantic Ocean during October–November 2002 were highly variable and range from 97 to 118%. The mean overall saturation was 104 ± 4%. Enhanced saturations were observed in the Guinea Dome area (up to 118%), in the equatorial upwelling (up to 109%), and the shallow continental shelf area off the West African Coast (up to 113%). Our results are in agreement with previously published data sets. We found a good correlation of seawater temperature with N_2O concentrations in the equatorial upwelling area. We conclude that the tropical North Atlantic Ocean is a net source of N_2O to the atmosphere with a pronounced regional variability.

[13] **Acknowledgments.** We thank A. Körtzinger and M. O. Andreae for technical support and acknowledge the help of the other M55 participants and the officers and crew of R/V *Meteor*. We especially thank R. Hoffmann for the calibration of our standards and two anonymous reviewers for their valuable comments. We are indebted to the authorities of Guinea-Bissau for permission to work in their territorial waters. The investigations were financially supported by the *Deutsche Forschungsgemeinschaft* through grants WA1434/1 and WA1434/3.

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